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Domino Mukaiyama–Michael reactions in the synthesis of polycyclic systems

Florence C. E. Sarabèr,[a] Svetlana Dratch,[b] Geke Bosselaar,[a] Ben J. M. Jansen[a] and Aede de Groot[a,*]

[a]*Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands*
[b]*Institute of Bioorganic Chemistry, National Academy of Sciences of Belarus, Kuprevich str. 5/2, 220141, Minsk, Belarus*

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Abstract—Good results were obtained in the Mukaiyama–Michael reaction of the silyl enol ether of cyclohexanone with 2-methyl-2-cyclopentenone and carvone, with transfer of the silyl group to the receiving enone and with $TrSbCl_6$ as catalyst. A second Mukaiyama–Michael reaction of this new silyl enol ether with methyl vinyl ketone and cyclization of the resulting adduct leads to tricyclic compounds in one-pot domino sequences. The scope and limitations of this domino reaction have been investigated.

1. Introduction

The usefulness of sequential Michael additions in domino reactions has been demonstrated several times[1–16] and also the Lewis acid-promoted Michael addition of silyl enol ethers to enones, originally devised by Mukaiyama et al. is a valuable tool in this field.[17,18] Recently it has been shown that an enantiomerically pure trans-hydrindane derivative can be synthesised using a double Mukaiyama–Michael reaction,[4,6] and also a highly substituted cyclohexene has been obtained in a domino reaction using a double Mukaiyama–Michael addition, followed by an intramolecular 1,6-aldol condensation.[1] It is evident that the intermediate enolate has to be preserved for such a sequence, so that the second Mukaiyama–Michael addition can take place. Transfer of the silyl group from the starting silyl enol ether to the receiving enone is in this respect a very convenient side reaction, which has been noticed early on to occur in some Mukaiyama–Michael additions.[10] This newly formed silyl enol ether can be isolated but can also be reacted further in one-pot in a second Mukaiyama–Michael addition, potentially with a different enone, or with other reagents.[1–11]

Based on these premises, the enantioselective construction of highly substituted polycyclic compounds should be possible starting with cyclic silyl enol ethers and cyclic enones using two consecutive Mukaiyama–Michael reactions followed by a ring-closing 1,6-aldol cyclization. To probe the feasibility of such an approach, first two reaction sequences starting with a cyclohexanone-derived silyl enol ether **1** in additions with carvone **2**, as a chiral receiving enone, and with 2-methyl-2-cyclopentenone **3** have been investigated. In both cases the intermediate adducts **4** have been reacted further with methyl vinyl ketone (MVK) **5** as the second enone (see Scheme 1). This should lead to adducts **6**, which can undergo an intramolecular 1,6-aldol condensation with the carbonyl group of the cyclohexanone moiety, which originates from the first silyl enol ether, to give the tricyclic endproducts **7**.

Variations in the starting silyl enol ether would open possibilities for further transformations of the tricyclic systems, which have potential as intermediates in the synthesis of polycyclic natural products. With carvone as the first receiving enone, stereochemical guiding of the configuration around the rings will be possible. The use of 2-methyl-2-cyclopentenone as the first receiving enone should give a tricyclic compound with possible use for the synthesis of steroid skeletons.

2. Results and discussion

To investigate the feasibility of the approach and to find the optimal conditions and stoichiometry for the reaction sequence mentioned in Scheme 1, several catalysts,

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* Corresponding author. Tel.: +31 317482370; fax: +31 317484914; e-mail: aede.degroot@wur.nl

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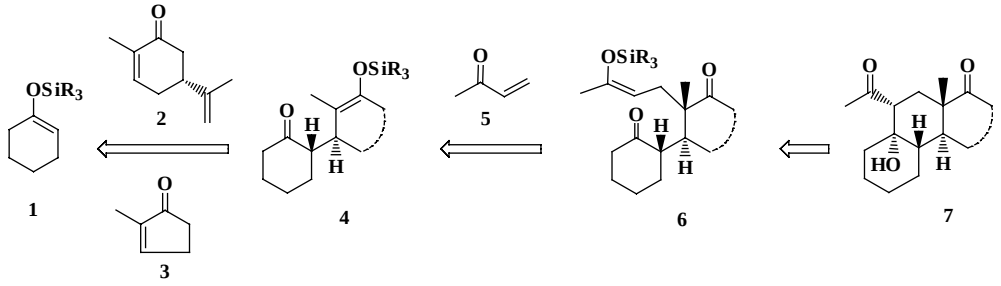
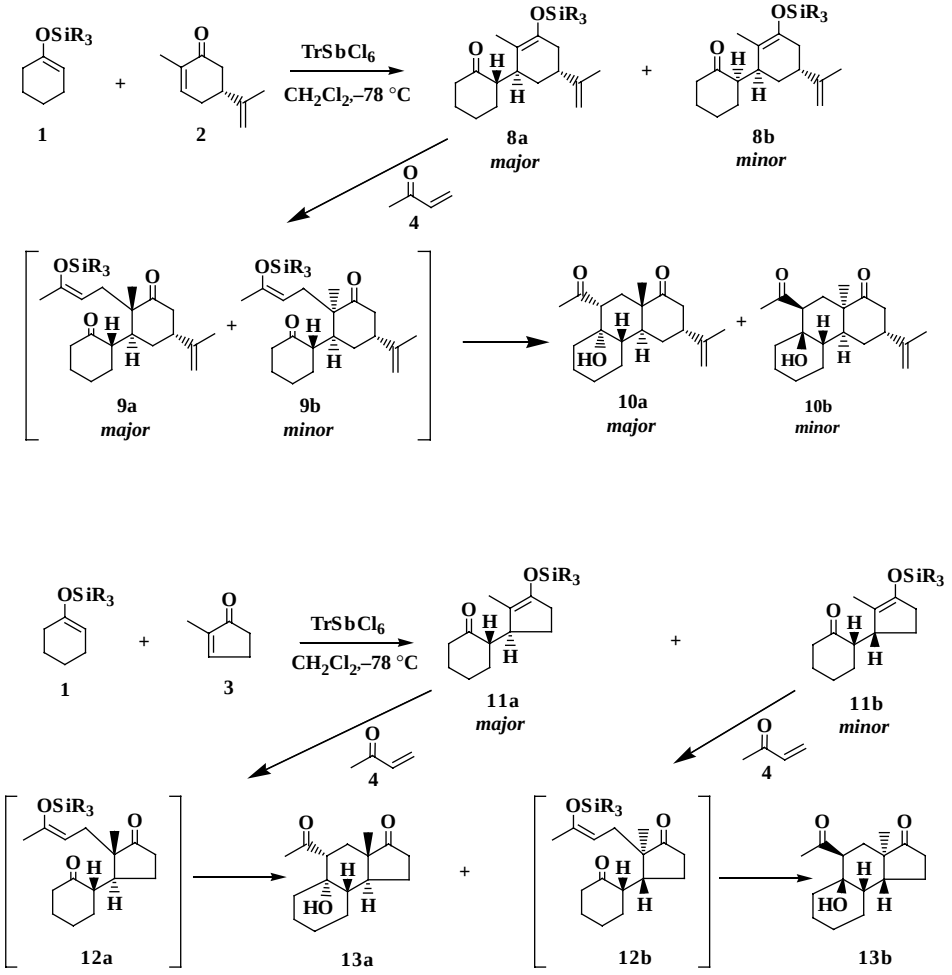


Scheme 1.

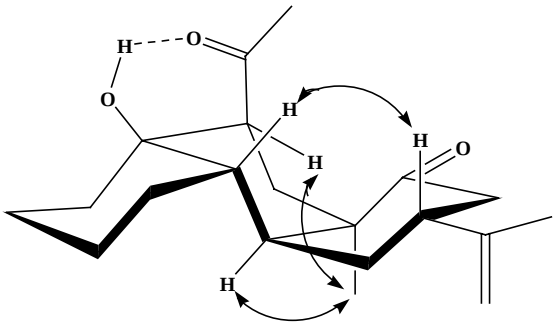
different addition orders, reaction temperatures and reagent ratios were researched. Many Lewis acids have been used as catalysts in Mukaiyama reactions but relatively few have been reported to give also transfer of the silyl group.[19–27] In our reaction, SmI_2, $TMSNTf_2$, $BuSn(OTf)_2$, $TrClO_4$ and $TrSbCl_6$ were investigated and the trityl salts were found to give the best results, as was expected from literature. Since $TrSbCl_6$ is commercially available and can be stored at $+4\,^{\circ}C$ without decomposition or loss of activity, this catalyst was chosen for all the following reactions. While the addition order of reagents and catalyst did not influence in any way the reaction yield or product ratios, the reaction temperature had to be kept low ($-78\,^{\circ}C$) to avoid hydrolysis of the starting silyl enol ether. At temperatures above $-60\,^{\circ}C$ an increase in desilylated starting material could clearly be detected on TLC. In the reaction of silyl enol ether **1** with carvone it was found that the use of 1, 1.25 or 1.5 equiv of **1** led to yields of 72, 82 and 89%, respectively, and therefore an excess of 1.5 equiv of silyl enol ether was applied in all reactions performed thereafter.

From both reaction sequences only two isomers of the final tricyclic products were isolated, and no other isomers were detected (see Scheme 2). The intermediate second adducts **9a**, **9b**, **12a** and **12b** have never been isolated because they reacted further to the tricyclic products under the applied conditions. The relative stereochemistry of compounds **10a**, **13a** and **13b** was determined by X-ray crystallography[28] and



Scheme 2.

for compound **10b** this was done using COSY and NOESY experiments (for the most important NOE interactions see Fig. 1), as this compound could not be obtained in a crystalline form. The position of the hydroxyl group was determined using IR-concentration experiments, showing an intramolecular H-bridge, between the hydroxy and the acetyl group.



10b

Figure 1.

The formation of the obtained products in the reaction with carvone can be explained by addition of the cyclohexanone silyl enol ether **1** from the less hindered side of the enone, opposite to the isopropenyl group. Epimeric mixtures of adducts are formed that differ in configuration only at C2 of the cyclohexanone moiety. The second addition of MVK **4** to the newly formed silyl enol ether takes place only with the major epimer. Steric factors probably are the reason for this difference but these factors are difficult to specify further. During this research it became clear that even small differences in steric hindrance can have significant influence on the yields and products of these Mukaiyama additions (see below). The second addition with MVK is not completely stereoselective, and occurs predominantly trans with respect to the cyclohexanone moiety. With 2-methyl-2-cyclopentenone as the receiving enone, diastereomeric racemates are obtained with trans-positioned substituents in the cyclopentanone part of the molecules. In this case, both products from the first addition (**11**) react further with MVK to afford tricyclic products.

Three silyl enol ethers with different steric effects (TMS, TBDMS and TES) were tested under the conditions mentioned above (1.5 equiv of silyl enol ether, 0.05 equiv of $TrSbCl_6$ as catalyst, at −78 °C). The reactions were quenched after the first Mukaiyama–Michael addition and then reacted further in a separate reaction with MVK, in order to get an impression of the stereoselectivity of the separate steps of the domino reaction. The TBDMS enol ether gave the best result in the reaction with carvone as the receiving enone (see Table 1), but the consecutive reaction with MVK gave a slightly better yield with the TMS enol ether. The reaction sequence with the TES enol ether gave only a moderate yield for the first addition step with carvone, and the domino reaction sequence gave a very low yield. This lower yield in the addition of the TES ether may be caused by a small increase in steric hindrance. The TES ether has less possibilities to minimize steric effects by rotation around the Si–O bond in comparison with the TBDMS ether. With 2-methyl-2-cyclopentenone as the receiving enone, no differences in yields between the TMS and TBDMS groups were found in the first step, but for the second Mukaiyama–Michael addition the best results were again obtained with the TMS enol ether. Apparently steric hindrance from the bulky TBDMS group has a greater influence in the second addition step, substantially lowering the yield in the five-membered ring compounds.

With respect to the stereoselectivity in the first step, the three silyl enol ethers all gave an addition to the enone of carvone opposite to the isopropenyl group, with comparable ratios of isomers in the cyclohexanone part of the molecules. In the consecutive MVK addition step, the reaction with the TBDMS enol ether led to the formation of only one isomer, thus giving a much higher stereoselectivity than the reaction with the TMS enol ether. The absence of steric hindrance in the starting enol ether gives the bulky TBDMS group the possibility to steer out of range, in this way not interfering with the approach to the enone for addition. When substituents are present in the neighbourhood of the enol ether moiety, the TBDMS group can not freely rotate and consequently its bulkiness interferes with the approach to the second enone (MVK) and influences the stereoselectivity of the reaction to a greater extent, which confirms the findings of Heathcock et al.[29,30]

In the TMS and in the TBDMS enol ether of the intermediate, the 2*S* isomer **8a** reacts much easier than the 2*R* isomer **8b**, as no final or intermediate product derived from the latter has been isolated.

In the Mukaiyama–Michael additions with 2-methyl-2-cyclopentenone, the bulkiness of the TBDMS enol ether already influences the stereoselectivity of the first Mukaiyama reaction, improving the isomer ratio to 4:1 in comparison with the almost 1:1 ratio for the TMS enol ether. However, in the second Mukaiyama–Michael addition with MVK, the higher stereoselectivity of the TBDMS enol ether shown in the first addition has disappeared and a much better selectivity was obtained with the TMS enol ether. A conceivable explanation could be that the TBDMS isomer **11a** reacts slower with MVK than isomer **11b**, possibly due

Table 1

Enone	Silyl group	Yield first addition (%)	Isomeric ratio (*a*:*b*)	Yield second addition (%)	Isomeric ratio (*a*:*b*)	Yield domino reaction (%)
2	TMS	89	2:1	49	5:1	45
2	TBDMS	94	2:1	45	1 (**10a**)	38
2	TES	46	3:2	—	—	5
3	TMS	85	6:5		4:1	61
3	TBDMS	83	4:1	—	2:1	32

All reactions have been carried out in duplicate.

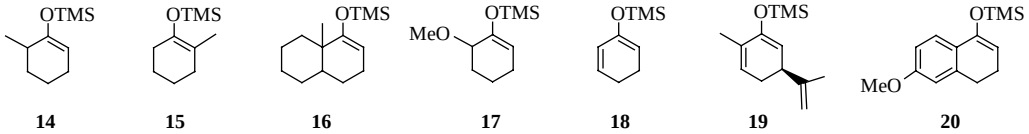


Figure 2.

to the higher steric strain in the latter, in combination with an easy desilylating side reaction in isomer **11a**. These factors could also explain the much lower yield for the domino reaction with the TBDMS enol ether (see below), pointing to a low-yielding second addition step. Interestingly, the MVK addition in the TMS enol ether resembles the one in the carvone route, having a strong preference for isomer **11a** of the intermediate, although in this case less pronounced.

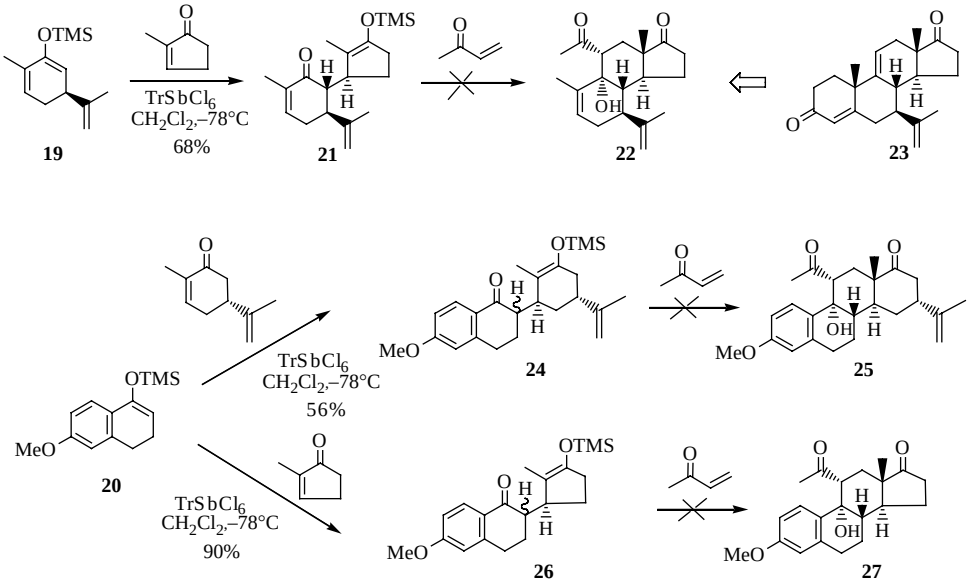
The reaction sequences were also performed as one-pot procedures, in which the second enone (MVK) was added at low temperature to the reaction mixture after completion of the first Mukaiyama–Michael addition. Although this domino reaction procedure[31] did not usually increase the overall yield dramatically, giving typically 40–50% of the tricyclic products, it did simplify the total reaction process considerably by taking out one complete purification step.

Variation in the starting silyl enol ether would give an impression about the scope and limitations of the domino sequence and maybe open up possibilities for enantioselective and short syntheses of steroids and D-homosteroids. For this reason, silyl enol ethers derived from cyclic ketones with more steric hindrance in the molecule (compounds **14–17**) or with a double bond or benzene ring conjugated with the carbonyl group (compounds **18** and **20**) were investigated (see Fig. 2) in their reactions with *R*-carvone as the first receiving enone and with MVK as the second enone. Compounds **19** and **20** were also reacted with 2-methyl-2-cyclopentenone as the first receiving enone, followed by addition of MVK (see Scheme 3).

An additional reason to select compounds **17–19** was to introduce functionality in the left ring, enabling further conversion of the tricyclic skeleton. The use of silyl enol ether **19** derived from (*S*)-(+)-carvone in an addition with 2-methyl-2-cyclopentenone as the receiving enone could possibly lead to an enantioselective synthesis of a tricyclic intermediate **22** that would enable completion of a steroid skeleton **23** (see Scheme 3). (D-homo) steroids could rapidly become accessible using silyl enol ether **20** derived from 6-methoxy-1-tetralone, a compound that has already been used extensively in steroid total synthesis.[32–38]

Although in the previous results with the cyclohexanone-derived silyl enol ethers, the TBDMS enol ether gave the best and most selective domino Mukaiyama–Michael addition, this silyl group proved not always to be the best choice. Sometimes the TBDMS enol ethers appeared troublesome to obtain or the first addition reaction gave no products. Therefore, the TMS enol ethers were used in all reaction sequences, which were carried out under the standart reaction conditions (1.5 equiv of silyl enol ether, 0.05 equiv of $TrSbCl_6$ as catalyst, at −78 °C). However, the overall results were disappointing.

The Mukaiyama–Michael addition of silyl enol ethers **14–16** to carvone proceeded in modest yields varying from 30 to 53%, but in all cases unseparable mixtures of stereoisomers were obtained. The reaction with the methoxy compound **17** did not proceed at all and the product from dienolsilyl enol ether **18**, proved to be unstable. The reaction of the carvone derived silyl enol ether **19** with 2-methyl-2-cyclopentenone led to product **21** in a reasonable 68% yield. It was published before that addition of the TMS enol ether



Scheme 3.

of 6-methoxytetralone **20** to carvone gave a 3:2 mixture of stereoisomers **24** in 56% yield, and that the stereoselectivity and the yield are dependent on the type of starting silyl enol ether. It was found also that the addition of **20** to 2-methyl-2-cyclopetenone gives a 2:1 mixtures of stereoisomers of **26** in 90% yield.[39]

In the consecutive addition reactions with MVK small amounts (24 and 14%) of tricyclic products were obtained from the product mixtures of silyl enol ethers resulting from **14** and **15**, respectively, but the stereochemistry of these products could not be established unambiguously. No reaction to tricyclic products was observed in all other cases and mostly only the desilylated intermediate adducts could be isolated. These results show again that the reaction sequence is sensitive for steric effects and especially the yields of the second addition reaction with MVK drop dramatically when extra substituents are present in the molecule.

The failure of the second addition with MVK in the silyl enol ethers **21**, **24** and **26** either could be caused by steric hindrance and/or by electronic effects in the 1,6-aldol cyclization due to electron delocalisation in the receiving enones. It seems that the electronic effects are the most important, as it appeared to be possible to react the intermediates **24** and **26** with carbocation precursors in irreversible reactions.[40] When the first carbonyl group is conjugated with a double bond or an aromatic system, the positive polarisation of the C-atom of the carbonyl group is less pronounced and hence this group is less reactive in aldol cyclizations. However, also uncyclised products similar to compound **6** never have been isolated. This can be explained by the equilibrium of the MVK addition lying on the side of the intermediates like **4**. Only if ring closure takes place, the equilibrium is shifted, finally to the tricyclic product. When ring closure does not take place, MVK will leave the molecule again and therefore almost no uncyclised products like **6**, or their desilylated equivalents, were found.

3. Experimental

3.1. General procedure

All reagents used were purchased from Aldrich or Acros, except for carvone, which was donated by Quest, and used without further purification unless otherwise stated. The used solvents were freshly distilled, except for benzene, which was stored over mol sieves (4 Å); dichloromethane was distilled over calcium hydride and tetrahydrofuran (THF) over sodium benzophenone ketyl. The glass equipment used was dried overnight in an oven of 150 °C and cooled down to room temperature under nitrogen. Reactions under dry conditions were performed under a steady flow of dry nitrogen or argon.

Reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel $60F_{254}$ plastic sheet plates and compounds were visualized by potassium permanganate or by acidic molybdate solution and subsequent heating. Product solutions were dried over Na_2SO_4 or $MgSO_4$ before evaporation under reduced pressure using a rotary evaporator. Column chromatography was performed with Fluka silica gel mean pore size 60 (SiO_2, 230–400 mesh) with mixtures of distilled petroleum ether, boiling range 40–60 °C (PE) and distilled ethyl acetate (EA) as eluents, unless reported otherwise. ^1H and ^{13}C NMR experiments were, unless otherwise stated, conducted on a Bruker AC-E 200, at 200 and 50 MHz, respectively, using $CDCl_3$ or C_6D_6 as solvents. Chemical shifts are reported in ppm (parts per million) (δ), referenced to residual $CHCl_3$ or C_6H_6 as internal standard, and coupling constants are expressed in Hz. ^1H NMR multiplicities are mentioned as singlet (s), doublet (d), triplet (t), quadruplet (q), broad singlet (br s), multiplet (m), double doublet (dd), etc. Multiplicities of the ^{13}C NMR signals were determined using the DEPT technique and are mentioned as q (CH_3), t (CH_2), d (CH) or s (C). When two isomers were detected and specific peaks could be assigned in the spectra, the data referred to the major isomer are marked as (*M*) and those of the minor isomer as (*m*). When the isomers are equally present, the data is presented as 14.35 and 17.87 (q). Melting points were determined on a C. Reichert, Vienna, hot stage apparatus, and are uncorrected. Infrared spectra were recorded on a FT-IR Biorad FTS-7 spectrometer using carbon tetrachloride (CCl_4) or chloroform ($CHCl_3$) as solvents when a solution was used. Only the characteristic absorptions were reported. The isomeric ratio of all the crude products was determined using GC–MS detection at 70 eV on a Hewlett Packard 5890B series Mass Selective Detector, coupled with a Hewlett Packard 5973 GC provided with a DB-17 fused silica capillary column, 30 m×0.25 mm i.d., film thickness 0.25 μm with helium as the carrier gas, programmed from 100–250 °C at a rate of 10 °C/min, followed by an isothermic period at 250 °C. MS and HRMS data were obtained with a Finnigan MAT 95 spectrometer. The ratios *m/e* and relative intensities (%) are indicated for significant peaks. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 20 °C in chloroform solutions and concentrations are specified in units of g/100 ml.

3.2. General method for thermodynamic silylation

3.2.1. (1-Cyclohexen-1-yloxy)(trimethyl)silane (1[TMS]).[41] To a stirred solution of cyclohexanone (2.45 g, 25 mmol) in CH_3CN (100 ml) under nitrogen were added Et_3N (5.56 ml, 40 mmol), TMSCl (4.32 g, 40 mmol) and NaI (6.00 g, 40 mmol), in this order. After overnight stirring at room temperature, the reaction mixture was diluted with PE (100 ml) and the acetonitrile layer was extracted with PE (2×100 ml). The combined organic layers were washed with a saturated $NaHCO_3$ solution (100 ml) and brine (100 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by bulb-to-bulb distillation (br pt 44 °C at 4 Torr) to give **1**[TMS] as a colourless liquid (3.32 g, 78%). IR (CCl_4 sol) cm^{-1} 2933, 1668, 1549, 1252; ^1H NMR ($CDCl_3$): −0.12 (s, 9H), 1.30–1.38 (m, 2H), 1.38–1.53 (m, 2H), 1.77–1.92 (m, 4H), 4.66–7.71 (m, 1H); ^{13}C NMR ($CDCl_3$): 0.3 (3q), 22.3 (t), 23.2 (t), 23.8 (t), 29.9 (t), 104.3 (d), 150.3 (s). HRMS: M^+, found 170.1123. $C_9H_{18}OSi$ requires 170.1127. MS *m/e* (%): 170 (M^+, 100), 169 (41), 155 (64), 142 (23), 127 (49), 75 (86), 73 (55). These data are in accordance with literature values.

3.2.2. *tert*-Butyl(1-cyclohexen-1-yloxy)dimethylsilane (1[TBDMS]).[42] See method description of compound **1**[TMS] for procedure and reaction scale. Yield: 83%, as a clear oil (br pt 55 °C at 0.3 Torr). IR (CCl_4 sol) cm^{-1}: 2931, 2859, 1668, 1549, 1254; ^1H NMR ($CDCl_3$): 0.01 (s, 9H), 0.12 (s, 6H), 1.45–1.59 (m, 2H), 1.59–1.72 (m, 2H), 1.94–2.08 (m, 4H), 4.85–4.90 (m, 1H); ^{13}C NMR ($CDCl_3$): −4.4 (q), −2.9 (q), 18.0 (s), 22.4 (t), 23.2 (t), 23.8 (t), 25.7 (q), 29.9 (t), 104.3 (d), 150.5 (s). HRMS: M^+, found 212.1598. $C_{12}H_{24}OSi$ requires 212.1596. MS *m/e* (%): 212 (M^+, 22), 75 (80), 73 (19). These data are in accordance with literature values.

3.2.3. (1-Cyclohexen-1-yloxy)(triethyl)silane (1[TES]).[43] See method description of compound **1**[TMS] for procedure and reaction scale. Yield: quantitative, as a colourless oil (br pt 54 °C at 0.5 Torr). IR (CCl_4 sol) cm^{-1}: 2956, 2877, 1667, 1550; ^1H NMR ($CDCl_3$): 0.60 (s, 9H), 0.60–0.88 (m, 6H), 1.50–1.58 (m, 2H), 1.58–1.71 (m, 2H), 1.96–2.00 (m, 4H), 4.84–4.87 (m, 1H); ^{13}C NMR ($CDCl_3$): 5.0 (q), 5.8 (t), 6.4 (t), 6.5 (q), 6.8 (q), 23.8 (t), 29.8 (t), 41.5 (t), 41.9 (t), 103.9 (d), 150.4 (s). HRMS: M^+, found 212.1598. $C_{12}H_{24}OSi$ requires 212.1596. MS *m/e* (%): 212 (M^+, 23), 169 (18), 156 (12), 155 (17), 103 (47), 75 (43). These data are in accordance with literature values.

3.2.4. 2-{(5*R*)-5-Isopropenyl-2-methyl-3[(trimethylsilyl)oxy]-2-cyclohexen-1-yl}cyclohexanone (8[TMS]). (*R*)-(−)-Carvone (150 mg, 1 mmol) and **1**[TMS] (255 mg, 1.50 mmol) were dissolved in dichloromethane (6 ml) and stirred under nitrogen. The reaction mixture was cooled to −78 °C. Trityl antimony hexachloride ($TrSbCl_6$) (29 mg, 0.05 mmol) was added and the reaction was followed by TLC. When all the carvone had reacted (1 h), the catalyst was quenched by adding a few drops of pyridine, until the yellow colour disappeared. The reaction mixture was allowed to warm to room temperature and diluted with dichloromethane (14 ml). The mixture was washed with a saturated $NaHCO_3$ solution (20 ml) and brine (20 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified on a short SiO_2 column (PE/EtOAc/pyridine 98:1:1) to give **8**[TMS] (286 mg, 89%) as a colourless oil composed of two isomers, which could not be separated, in a ratio of 2:1 (GC). IR (film) cm^{-1}: 2936, 1709, 1644, 1251; ^1H NMR ($CDCl_3$): 0.15 (s, 9H), 1.53 (s, 3H), 1.52–1.69 (m, 5H), 1.69 (s, 3H), 1.91–2.07 (m, 4H), 2.20–2.40 (m, 4H), 2.90–2.92 (m, 1H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$): 0.8 (3q), 17.5 (q), 20.5 (q), 25.4 (*M*) and 27.1 (*m*) (t), 27.9 (*M*) and 28.6 (*m*) (t), 29.2 (*m*) and 32.6 (*M*) (t), 33.7 (t), 35.1 (t), 35.7 (d), 37.8 (*M*) and 39.2 (*m*) (d), 42.4 (t), 52.9 (*m*) and 56.3 (*M*) (d), 109.0 (t), 112.9 (s), 144.9 (s), 148.7 (*m*) and 148.9 (*M*) (s), 212.4 (s). HRMS: M^+, found 320.2173. $C_{19}H_{32}O_2Si$ requires 320.2172. MS *m/e* (%): 320 (M^+, 100), 181 (12), 75 (5), 73 (33).

3.2.5. 2-{(5*R*)-3-{[*tert*-Butyl(dimethyl)silyl]oxy}-5-isopropenyl-2-methyl-2-cyclohexen-1-yl}cyclohexanone (8[TBDMS]). See method description of compound **8**[TMS] for procedure and reaction scale. Yield: 94%, as a colourless oil (mixture of 2 isomers, 2:1). IR (film) cm^{-1}: 2932, 1710, 1678, 1449, 1254; ^1H NMR ($CDCl_3$): 0.11 (s, 6H), 0.88 (*m*) and 0.94 (*M*) (s, 9H), 1.52–1.72 (m, 5H), 1.51 (*m*) and 1.54 (*M*) (s, 3H), 1.69 (*M*) and 1.70 (*m*) (s, 3H), 1.85–2.11 (m, 5H), 2.12–2.50 (m, 4H), 2.86 (s, 1H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$): −3.7 (2q), 14.4 (*m*) and 17.9 (*M*) (q), 18.2 (s), 20.5 (*M*) and 20.7 (*m*) (q), 25.4 (t), 25.9 (3q), 27.2 (*m*) and 28.0 (*M*) (t), 28.7 (*M*) and 29.3 (*m*) (t), 32.7 (*m*) and 33.6 (*M*) (t), 35.1 (*m*) and 35.3 (*M*) (t), 35.8 (*m*) and 36.1 (*M*) (d), 37.8 (*M*) and 39.3 (*m*) (d), 42.2 (*m*) and 42.4 (*M*) (t), 52.9 (*m*) and 56.4 (*M*) (d), 109.0 (t), 111.4 (*m*) and 112.6 (*M*) (s), 145.0 (s), 148.7 (*m*) and 148.9 (*M*) (s), 212.6 (*M*) and 212.8 (*m*) (s). HRMS: M^+, found 362.2652. $C_{22}H_{38}O_2Si$ requires 362.2641. MS *m/e* (%): 362 (M^+, 9), 305 (2), 155 (10), 75 (12), 73 (31).

3.2.6. 2-{(5*R*)-5-Isopropenyl-2-methyl-3-[(triethylsilyl)oxy]-2-cyclohexen-1-yl}cyclohexanone (8[TES]). See method description of compound **8**[TMS] for procedure and reaction scale. Yield: 46%, as a colourless oil (2 isomers, 3:2). IR (film) cm^{-1}: 2936, 1710, 1449, 1238; ^1H NMR (C_6D_6): 0.64 (q, $J=7.9$ Hz, 6H), 0.97 (t, $J=7.9$ Hz, 9H), 1.53 (*m*) and 1.56 (*M*) (s, 3H), 1.70 (s, 3H), 1.45–1.71 (m, 5H), 1.88–2.12 (m, 4H), 2.26–2.45 (m, 4H), 2.89 (m, 1H), 4.70 (s, 2H); ^{13}C NMR (C_6D_6): 5.9 (3t), 6.9 (3q), 14.9 (*m*) and 17.6 (*M*) (q), 20.4 (*M*) and 20.7 (*m*) (q), 25.2 (t), 26.9 (*m*) and 27.6 (*M*) (t), 28.6 (*m*) and 32.4 (*M*) (t), 29.2 (*m*) and 33.7 (*M*) (t), 35.2 (*m*) and 35.5 (*M*) (t), 35.6 (*m*) and 36.1 (*M*) (d), 38.1 (*M*) and 39.5 (*m*) (d), 41.9 (t), 53.5 (*m*) and 56.1 (*M*) (d), 109.2 (t), 113.1 (s), 145.9 (s), 149.2 (*m*) and 149.6 (*M*) (s), 210.6 (*M*), 210.7 (*m*) (s). HRMS: M^+, found 362.2648. $C_{22}H_{38}O_2Si$ requires 362.2641. MS *m/e* (%): 362 (M^+, 26), 333 (9), 239 (12), 115 (13), 87 (24), 59 (11).

3.2.7. (3*R*)-9-Acetyl-8a-hydroxy-3-isopropenyl-10a-methyldodecahydro-1(2*H*)-phenanthrenone (10). *Mukaiyama–Michael addition of intermediate* **8**[TMS] *with MVK*. A stirred solution of $TrSbCl_6$ (29 mg, 0,05 mmol) in dichloromethane (10 ml) under nitrogen was cooled to −78 °C. A solution of **8**[TMS] (320 mg, 1 mmol) and methyl vinyl ketone (MVK, 0.17 ml, 2 mmol) in dichloromethane (5 ml) was added dropwise over a period of 2.5 h. The reaction mixture was stirred at −78 °C for another 2 h and was then allowed to warm to room temperature. Water (10 ml) was added and, after stirring for a further 1 h, the reaction mixture was diluted with dichloromethane (20 ml) and washed with a saturated $NaHCO_3$ solution (20 ml) and brine (20 ml). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (PE/EtOAc 9:1) to give two isomers **10a** (122 mg, crystals) and **10b** (25 mg, colourless oil) in a total 49% yield in a 5:1 ratio. Compound **10a** was recrystallised from pentane to give white needles.

Mukaiyama–Michael addition of intermediate **8**[TBDMS] *with MVK*. The reaction of **8**[TBDMS] (362 mg, 1 mmol) with MVK was carried out as described for **8**[TMS]. Compound **10a** (143 mg) was obtained as a single isomer in 45% yield as white crystals (needles) after recrystallisation from pentane.

Domino Mukaiyama reaction of **1**[TMS]. At room temperature, (*R*)-(−)-carvone (450 mg, 3 mmol) was added to a stirred solution of **1**[TMS] (765 mg, 4.5 mmol) in dichloromethane (20 ml) under nitrogen. The solution was cooled to −78 °C and $TrSbCl_6$ was added (87 mg, 0.15 mmol). After

2.5 h of stirring at −78 °C MVK (0.5 ml, 6 mmol) was added dropwise over a period of 3.5 h. The reaction mixture was stirred for another 2 h at −78 °C, before slow warming to room temperature overnight. No TLC control was done during the reaction due to the sensitivity of the compounds towards desilylation. Water (10 ml) was added and after further stirring for 1 h the reaction mixture was diluted with dichloromethane (20 ml). The organic layer was washed with a saturated $NaHCO_3$ solution (20 ml) and brine (20 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (PE/EA 20:1, with 1% pyridine) to give a total 45% yield of **10a** (119 mg) and **10b** (24 mg) in a 5:1 ratio.

Domino Mukaiyama reaction of **1**[TBDMS]. The reaction of **1**[TBDMS] (954 mg, 4.5 mmol) was carried out as described for **1**[TMS]. Compound **10a** (120 mg) was obtained as a single isomer in 38% yield as white crystals (needles) after recrystallisation from pentane.

Compound **10a**. Mp 68–72 °C (from pentane); IR (CCl_4 sol) cm^{-1}: 3488, 2937, 1707, 1252; ^1H NMR ($CDCl_3$): 1.01–1.22 (2H, m), 1.18 (3H, s), 1.22–1.48 (4H, m), 1.55–1.84 (9H, m), 1.88–2.13 (2H, m), 2.19 (3H, s), 2.35–2.55 (2H, m), 2.64 (d, $J=6.7$ Hz, 1H), 3.02 (dd, $J_1=3.3$ Hz, $J_2=9.9$ Hz, 1H), 3.99 (OH), 4.65 (1H, s), 4.81 (1H, s); ^{13}C NMR ($CDCl_3$): 19.9 (q), 22.3 (q), 23.8 (t), 25.7 (t), 26.4 (t), 26.9 (t), 31.6 (q), 31.9 (t), 33.6 (d), 38.8 (t), 40.5 (d), 41.1 (t), 45.6 (d), 47.4 (s), 48.2 (d), 72.1 (s), 112.5 (t), 146.6 (t), 214.6 (s), 215.4 (s). HRMS: M^+, found 318.2203. $C_{20}H_{30}O_3$ requires 318.2195. MS *m/e* (%): 318 (M^+, 42), 248 (86), 221 (63), 204 (96), 179 (77), 161 (84), 151 (98), 98 (67).

Compound **10b**. IR (CCl_4 sol) cm^{-1}: 3488, 2937, 1707, 1252; ^1H NMR ($CDCl_3$): 1.14 (3H, s), 1.04–1.28 (2H, m), 1.32–1.85 (13H, m), 1.93–2.12 (2H, m), 2.17 (3H, s), 2.50–2.62 (2H, m), 2.62–2.74 (2H, m), 3.67 (OH), 4.69 (1H, s), 4.80 (1H, s); ^{13}C NMR ($CDCl_3$): 16.9 (q), 20.7 (t), 21.5 (q), 23.7 (t), 25.3 (t), 26.1 (t), 31.4 (q), 32.1 (t), 36.3 (d), 37.5 (t), 39.4 (d), 40.7 (t), 42.8 (d), 47.2 (s), 53.3 (d), 70.8 (s), 112.0 (t), 146.8 (s), 215.7 (s), 215.9 (s). HRMS: M^+, found 318.2203. $C_{20}H_{30}O_3$ requires 318.2195. MS *m/e* (%): 318 (M^+, 42), 248 (86), 221 (63), 204 (96), 179 (77), 161 (84), 151 (98), 98 (67).

3.2.8. 2-{2-Methyl-3-[(trimethylsilyl)oxy]-2-cyclopenten-1-yl}cyclohexanone (11[TMS]). 2-Methyl-2-cyclopentenone (384 mg, 4 mmol) and **1**[TMS] (1.36 g, 8 mmol) were dissolved in dichloromethane (25 ml) and stirred under nitrogen. The reaction mixture was cooled to −78 °C. Trityl antimony hexachloride ($TrSbCl_6$) (58 mg, 0.05 mmol) was added and the reaction was followed by TLC. When all the carvone had reacted (1 h), the catalyst was quenched by adding a few drops of pyridine, until the yellow colour disappeared. The reaction mixture was allowed to warm to room temperature and diluted with dichloromethane (15 ml). The mixture was washed with saturated $NaHCO_3$ solution (25 ml) and brine (25 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified on a short column (PE/EtOAc/pyridine 98:1:1) to give **11**[TMS] (906 mg, 85%) as a colourless oil composed of two isomers, which could not be separated, in a ratio of 6:5. IR (film) cm^{-1}: 2937, 2860, 1709, 1691, 1330, 1252, 1211; ^1H NMR ($CDCl_3$): 0.01 (s, 9H), 1.24 (s, 3H), 1.11–2.38 (m, 13H), 2.86–3.09 (m, 1H); ^{13}C NMR ($CDCl_3$): 0.6 (3q), 10.1 (*M*) and 12.1 (*m*) (q), 22.9 (t), 24.9 (*M*) and 25.4 (*m*) (t), 26.5 (*M*) and 27.0 (*m*) (t), 27.2 (*M*) and 28.5 (*m*) (t), 32.6 (*m*) and 33.2 (*M*) (t), 42.0 (*m*) and 42.2 (*M*) (t), 42.7 (*m*) and 43.2 (*M*) (d), 52.3 (*M*) and 54.8 (*m*) (d), 113.1 (*M*) and 114.4 (*m*) (s), 147.7 (*M*) and 148.3 (*m*) (s), 211.9 (*m*) and 212.8 (*M*) (s). MS *m/e* (%): 266 (M^+, 2), 169 (100), 155 (3), 75 (11), 73 (66).

3.2.9. 2-(3-{[*tert*-Butyl(dimethyl)silyl]oxy}-2-methyl-2-cyclopenten-1-yl)cyclohexanone (11[TBDMS]). See method description of compound **11**[TMS] for procedure and reaction scale. Yield: 83%, as a colourless oil (2 isomers, 4:1). IR (CCl_4 sol) cm^{-1}: 2923, 2858, 1711, 1549, 1253; ^1H NMR ($CDCl_3$): 0.10 (s, 6H), 0.93 (s, 9H), 1.31–1.52 (m, 5H), 1.54–1.70 (m, 2H), 1.79–2.53 (m, 9H), 3.09 (s, 1H); ^{13}H NMR ($CDCl_3$) −4.0 (2q), 10.1 (q), 18.1 (s), 22.9 (t), 25.1 (t), 25.7 (3q), 26.5 (t), 27.2 (t), 33.2 (t), 42.4 (t), 43.1 (d), 52.4 (d), 112.7 (s), 147.9 (s), 213.1 (s). HRMS: M^+, found 308.2178. $C_{18}H_{32}O_2Si$ requires 308.2172. MS *m/e* (%): 308 (M^+, 14), 75 (25), 73 (33).

3.2.10. 5-Acetyl-5a-hydroxy-3a-methyldodecahydro-3*H*-cyclopenta[*a*]naphthalen-3-one (13). For general procedures and scale see the syntheses of **10**. From **11**[TMS] a total yield of 161 mg (61%), of **13a** and **13b** was obtained as white crystals in a 4:1 ratio, respectively. From **11**[TBDMS] a total yield of 84 mg (32%) of **13a** and **13b** was obtained in a 2:1 ratio, respectively.

Compound **13a**. Mp 86–90 °C (from pentane); IR (CCl_4 sol) cm^{-1}: 3469, 2933, 2860, 1739, 1692, 1398, 1359, 1190; ^1H NMR ($CDCl_3$): 0.92 (s, 3H), 1.08–2.18 (m, 15H), 2.18 (s, 3H), 2.41 (dd, $J_1=8.0$ Hz, $J_2=16.4$ Hz, 1H), 2.61 (dd, $J_1=5.1$ Hz, $J_2=11.5$ Hz, 1H), 3.81 (s, 1H); ^{13}C NMR ($CDCl_3$): 13.4 (q), 21.1 (2t), 23.4 (t), 25.7 (t), 31.3 (q), 31.8 (t), 35.7 (t), 37.0 (t), 42.8 (d), 42.9 (d), 47.2 (s), 53.7 (d), 72.0 (s), 215.9 (s), 219.5 (s). HRMS: M^+, found 264.1724. $C_{16}H_{24}O_3$ requires 264.1725. MS *m/e* (%): 264 (M^+, 2), 246 (9), 249 (8), 246 (10), 203 (18), 194 (54), 98 (100), 97 (92), 55 (18), 43 (15).

Compound **13b**. Mp 79–82 °C (from pentane); ^1H NMR ($CDCl_3$): 1.05 (s, 3H), 1.05–1.55 (m, 5H), 1.64–1.93 (m, 9H), 2.12 (dd, $J_1=8.5$ Hz, $J_2=19.1$ Hz, 1H), 2.24 (s, 3H), 2.32–2.57 (m, 1H), 3.10 (dd, $J_1=5.1$ Hz, $J_2=11.1$ Hz, 1H), 4.19 (s, 1H); ^{13}C NMR ($CDCl_3$): 16.9 (q), 20.8 (t), 24.0 (t), 25.7 (t), 26.1 (t), 31.5 (q), 31.7 (t), 35.7 (t), 38.8 (t), 41.6 (d), 46.3 (2d), 46.6 (s), 73.1 (s), 215.4 (s), 219.0 (s). HRMS: M^+, found 264.1726. $C_{16}H_{24}O_3$ requires 264.1725. MS *m/e* (%): 264 (M^+, 20), 249 (15), 246 (22), 221 (7), 203 (33), 194 (99), 98 (93). 97 (100), 43 (29).

3.2.11. {[(3*S*)-3-Isopropenyl-6-methyl-cyclohexa-1,5-dienyl]oxy}(trimethyl)silane (19[TMS]).[44] A solution of diisopropylamine (2.25 ml, 16 mmol) in THF (20 ml) was cooled to −10 °C, and butyllithium (1.45 M in THF, 10 ml) was added in one portion. The solution was allowed to warm to 0 °C and stirred for 30 min, after which the solution was cooled to −78 °C and a solution of (*S*)-(+)-carvone (2.0 g, 13.2 mmol) in THF (20 ml) was added dropwise over a period of 30 min. The solution was kept at −78 °C and

stirred for 20 min, followed by dropwise addition of TMSCl (2.0 ml, 16 mmol) over a period of 10 min. The solution was allowed to warm to room temperature over a period of 1 h and poured in a cold solution of brine and $NaHCO_3$ (10%). The water-layer was extracted with petrol-ether, and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. The crude product was purified by bulb-to-bulb distillation yielding 2.76 g of **19**[TMS] (94%) s a colourless oil. IR (CCl_4 sol) cm^{-1} 2963, 1660, 1605, 1550, 1451, 1375, 1253, 1214; ^1H NMR ($CDCl_3$): 0.18 (s, 9H), 1.67 (s, 3H), 1.71 (s, 3H), 2.11 (m, 2H), 2.99 (m, 1H), 4.69 (m, 1H), 4.76 (m, 2H), 5.54 (m, 1H); ^{13}C NMR ($CDCl_3$): 0.1 (3q), 17.3 (q), 20.5 (q), 28.6 (t), 41.8 (d), 105.7 (d), 109.9 (t), 123.0 (d), 131.8 (s), 148.4 (s), 149.8 (s). HRMS: M^+, found 222.1439. $C_{13}H_{22}OSi$ requires 222.1440. MS *m/e* (%): 222 (100, M^+), 207 (83), 181 (65), 165(62), 91 (24), 82 (17), 75 (21), 73 (79), 45 (16). Data are in accordance with literature values.

3.2.12. [(6-Methoxy-3,4-dihydro-1-naphthalenyl)oxy]-(trimethyl)silane (20[TMS]).[45] See method description of compound **1** for procedure and reaction scale. Yield: 92%, as a colourless oil. IR (CCl_4 sol) cm^{-1}: 2958, 2835, 1683, 1639, 1607, 1252; ^1H NMR δ: 0.31 (s, 9H), 2.24–2.35 (m, 2H), 2.79 (t, $J=7.8$ Hz, 2H), 3.83 (s, 3H), 5.12 (t, $J=4.6$ Hz, 1H), 6.74 (s, 1H), 6.76 (d, $J=8.6$ Hz, 1H), 7.41 (d, $J=8.2$ Hz, 1H); ^{13}C NMR δ: 0.2 (3q), 22.2 (t), 28.7 (t), 55.1 (q), 102.9 (d), 110.7 (d), 113.2 (d), 123.1 (d), 126.6 (s), 138.9 (s), 147.9 (s), 158.9 (s). HRMS: M^+, found 248.1229. $C_{14}H_{20}O_2Si$ requires 248.1233. MS *m/e* (%): 248 (M^+, 100), 247 (64), 233 (30), 217 (13), 73 (21). Data are in accordance with literature values.

3.2.13. 2-{(1*S*,5*R*)-5-Isopropenyl-2-methyl-3-[(trimethylsilyl)oxy]-2-cyclohexen-1-yl}-6-methoxy-3,4-dihydro-1(2*H*)-naphthalenone (24). See method description of compound **8** for procedure and reaction scale. Yield: 56%, as a mixture of 2 isomers (3:2), white crystals (mp 55–56 °C from pentane). IR (CCl_4) cm^{-1}: 2939, 1680, 1602, 1252; ^1H NMR δ: 0.15 and 0.19 (s, 9H), 1.39 and 1.58 (s, 3H), 1.68 and 1.73 (s, 3H), 1.45–2.65 (m, 7H), 2.75 (dt, $J_1=13.0$ Hz, $J_2=3.7$ Hz, 1H), 2.91–2.93 (m, 2H), 3.23 and 3.35 (br s, 1H), 3.83 (s, 3H), 4.72–4.74 (m, 2H), 6.67 (br s, 1H), 6.80 (dd, $J_1=8.7$ Hz, $J_2=2.5$ Hz, 1H), 8.02 (d, $J=8.7$ Hz, 1H); ^{13}C NMR (isomer 1) δ: 1.3 (3q), 11.9 (q), 21.4 (q), 25.5 (t), 27.2 (t), 28.1 (t), 34.4 (d), 40.6 (d), 42.2 (t), 46.6 (d), 55.4 (q), 77.0 (s), 111.7 (t), 112.3 (d), 113.4 (d), 125.9 (s), 129.9 (d), 145.6 (s), 146.7 (s), 163.5 (s), 198.9 (s), 213.8 (s); (isomer 2) 1.9 (3q), 12.2 (q), 21.1 (q), 26.8 (t), 29.1 (t), 29.5 (t), 36.5 (d), 42.4 (d), 44.1 (t), 47.9 (d), 55.4 (q), 77.7 (s), 111.0 (t), 112.3 (d), 113.2 (d), 125.2 (s), 130.0 (d), 145.8 (s), 147.0 (s), 163.5 (s), 198.8 (s), 213.8 (s). HRMS: M^+, found 398.2275. $C_{24}H_{34}O_3Si$ requires 398.2277. MS *m/e* (%): 398 (M^+, 12), 329 (3), 248 (31), 223 (100), 222 (49), 176 (21), 73 (33).

3.2.14. (5*S*,6*R*)-5-Isopropenyl-2-methyl-6-(2-methyl-3-trimethylsilanyloxy-cyclopent-2-enyl)-cyclohex-2-enone (24). The reaction was carried out as described for compound **11**. The reaction was carried out several times on a scale that varied from 100 mg to 1 g. The product was obtained in an average of 68% yield as a colourless oil. IR (CCl_4) cm^{-1}: 2960, 2957, 2945, 1741, 1671; ^1H NMR ($CDCl_3$): −0.01 (s, 9H), 1.28 (s, 3H), 1.51 (s, 3H), 1.54 (s, 3H), 1.15–2.68 (m, 9H), 4.59 (s, 2H), 6.38–6.44 (m, 1H); ^{13}C NMR ($CDCl_3$): 0.6 (3q), 10.7 (q), 15.6 (q), 18.8 (q), 22.9 (t), 30.3 (t), 32.6 (t), 45.1 (d), 46.2 (d), 50.0 (d), 113.0 (t), 114.8 (s), 136.1 (s), 142.0 (d), 146.1 (s), 146.5 (s), 200.3 (s). HRMS: M^+, found 318.2017. $C_{19}H_{30}O_2Si$ requires 318.2015. MS *m/e* (%): 318 (M^+, 9), 222 (15), 182 (6), 169 (100), 150 (5), 73 (34).

3.2.15. 6-Methoxy-2-(2-methyl-3-trimethylsilanyloxy-cyclopent-2-enyl)-3,4-dihydro-2*H*-naphthalen-1-one (26). See method description of compound **11** for procedure and reaction scale. Yield: 90%, as a colourless oil (2 isomers, 2:1). IR (CCl_4 sol) cm^{-1}: 2941, 2851, 1673, 1600, 1333, 1252; ^1H NMR ($CDCl_3$) δ: 0.14 (*M*) and 0.18 (*m*) (s, 9H), 1.27 (*M*) and 1.50 (*m*) (s, 3H), 1.41–2.73 (m, 7H), 2.86–3.00 (dd, $J_1=3.7$ Hz, $J_2=8.3$ Hz, 2H), 3.40–3.55 (*m*) and 3.55–3.65 (*M*) (m, 1H), 3.83 (s, 3H), 6.66 (d, $J=2.5$ Hz, 1H), 6.81 (dd, $J_1=2.5$ Hz, $J_2=8.7$ Hz, 1H), 8.00 (*m*) and 8.01 (*M*) (d, $J=8.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ: 0.6 (3q), 10.3 (*m*) and 11.9 (*M*) (q), 22.4 (*m*) and 23.6 (*M*) (t), 22.9 (*m*) and 25.0 (*M*) (t), 29.8 (*M*) and 29.9 (*m*) (t), 32.9 (*M*) and 33.1 (*m*) (t), 43.3 (*M*) and 43.9 (*m*) (d), 49.7 (*m*) and 52.2 (*M*) (d), 55.4 (q), 112.4 (d), 113.0 (d), 114.4 (s), 126.5(*M*) and 127.1 (*m*) (s), 129.7 (*m*) and 123.0 (*M*) (d), 146.5 (*M*) and 146.8 (*m*) (s), 147.9 (*m*) and 148.1 (*M*) (s), 163.3 (s), 197.8 (*M*) and 199.0 (*m*) (s). HRMS: M^+, found 344.1807. $C_{20}H_{28}O_3Si$ requires 344.1808. MS *m/e* (%): 344 (M^+, 9), 249 (8), 248 (34), 138 (8), 176 (36), 170 (15), 169 (100).

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